
App'n of Yale University and the University of South Carolina, jointly: YA-0002A

Appendix I

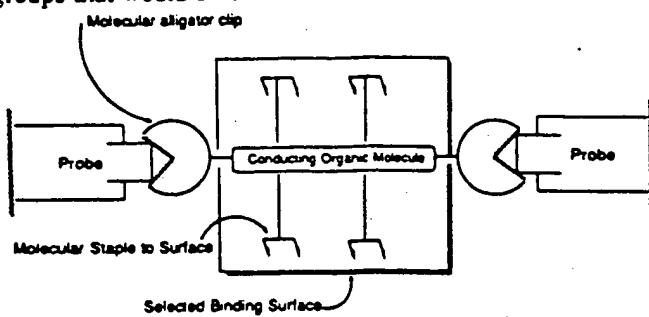
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Synthesis of Molecular Wires by a Novel Divergent/Convergent Approach

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Since the time of the first room-filling computers, there has been a tremendous drive to compress the size of computing instruments. In order to bring this desire to its extreme, it was conceived that one may be able to construct a single molecule that could function as a self-contained electronic device.¹ We have identified an approach which would allow the rapid synthesis of conjugated oligomers ("molecular wires") through the use of a novel divergent/convergent synthetic approach. Here we outline a methodology that should permit the rapid synthesis of molecular wires with dimensions needed for adhesion between a patterned electronic assembly. Hence, the feasibility of conduction on single or small molecular arrays may soon be experimentally addressed.

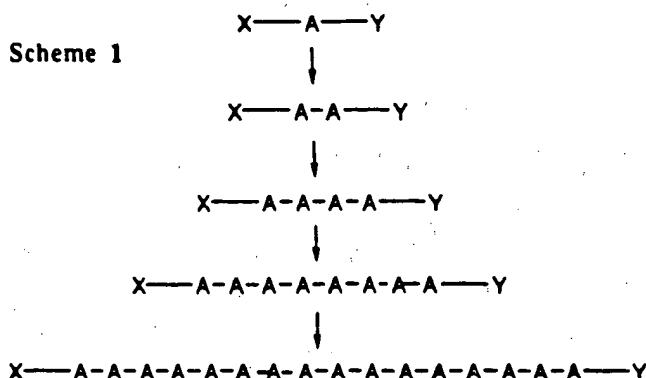
A schematic representation of the conducting system that we hope to construct is shown below. The nonfabricated portion will consist of two metallic probes on opposite sides of a selected binding surface. The target molecules may be spontaneously deposited, by self-assembly, from solution onto the binding surface and will bridge the gap between the metallic contacts by selectively attaching to the two metal probes. Ultimately, the "molecular alligator clips" will be, for example, thiols which will bind to gold probes while the "molecular staples" could be hydroxyl groups that would bind to an oxide surface below.



The conjugated oligomers that we are constructing are well-defined homogeneous materials that are fully characterized. We hope to ultimately construct oligomers $\sim 100 \text{ \AA}$ long; on the order of the resolution of current patterning techniques. Additionally, we hope to construct oligomers that are air and light stable to facilitate the assembly and fabrication.

An outline of the synthetic sequence is shown in Scheme 1. The synthesis of the oligomers begins with the formation of a monomer unit with different functional groups on the ends. The ends must be complimentary so that they will undergo a coupling reaction to give a dimeric species. The dimer would then be divided into two portions, the ends converted to the aforementioned complimentary end units, then coupled to afford the tetrameric species. This process would then continue until the desired length of "molecular wire" is reached by doubling the length of the

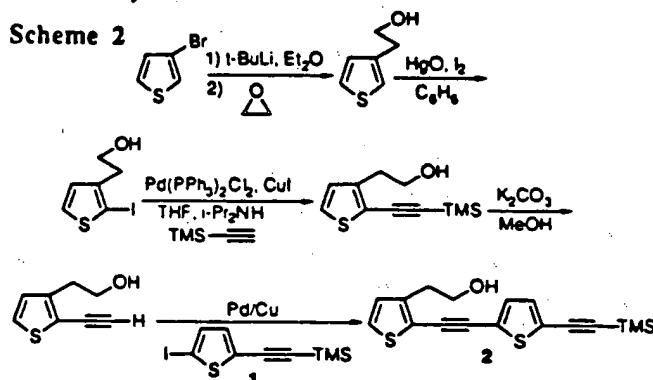
Scheme 1



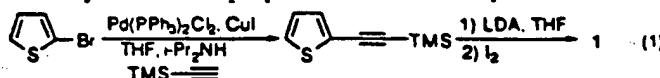
oligomer at each coupling stage.

The synthesis of the first oligomer (Scheme 2) began

Scheme 2



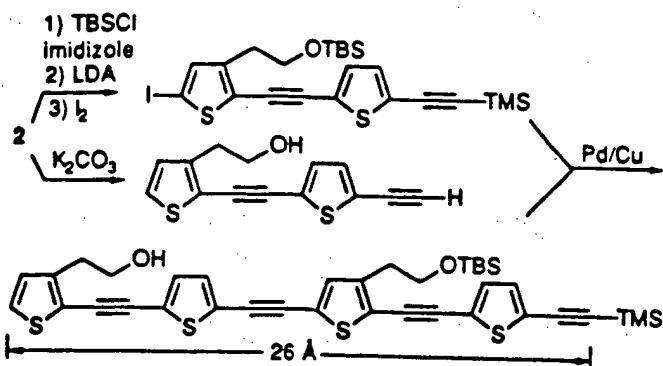
with the conversion of 3-bromothiophene to the hydroxyethyl derivative by the use of *t*-butyllithium and ethylene oxide. The subsequent alcohol was cleanly iodinated by the procedure of Uhlenbroek² in 81% yield. The iodide was then coupled with trimethylsilylacetylene in the presence of Pd(0) and Cu(I) in 81% yield.³ The new alkyne was then deprotected with K₂CO₃ in methanol and coupled with alkyne 1 in the presence of a Pd(0)/Cu(I) catalyst to afford 2 in 51% yield. 1 was prepared as shown in eq 1.



It was necessary to take one half of 2 and protect the alcohol in order to cleanly iodinate the terminal thiophene unit. A second portion of 2 had the terminal trimethylsilyl unit removed with fluoride and the two halves are then coupled under Pd(0)/Cu(I) conditions³ to afford the tetramer (Scheme 3). We experienced some problems with decomposition of the free acetylene at the dimer stage and again upon deprotection of the tetramer. This problem occurred regardless of the method of deprotection (K₂CO₃/MeOH or TBAF/THF) on the dimer and tetramer. Oxidative coupling afforded a head-to-head dimer $\sim 50 \text{ \AA}$ long. Based on these results, we began investigating a phenylene-ethynylene system which should be more stable to air but would still allow for the divergent/convergent synthetic approach.

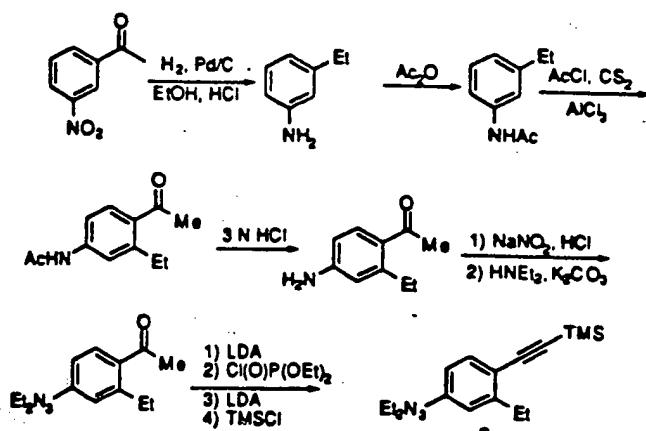
The synthesis of the phenylene-ethynylene monomer is shown in Scheme 4. Reduction of 3'-aminoacetophenone is

Scheme 3



afforded a nearly quantitative yield of the 3-ethylaniline which was protected with acetic anhydride in 86% yield (over 2 steps). The acylation was accomplished in 50% yield after purification by flash chromatography.⁴ The acetamide was then deprotected with hot 3 N HCl in quantitative yield.⁵ The next step in the synthetic sequence was the functional interconversion of the amine to a group that could function both as a protecting group and be converted to a halogen for cross-coupling. Moore has shown that amines can be converted to triazenes through the diazonium ion.⁶ This was accomplished with NaNO2 followed by quenching with HNEt2 to afford the triazene in 95% yield. The ketone was then converted to the silylalkyne 3 via the phosphate enolate.⁷

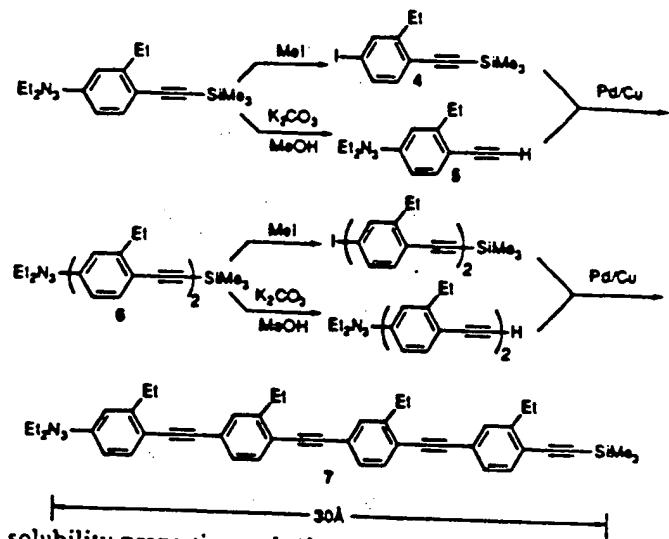
Scheme 4



With the synthesis of the monomer unit 3 completed, the divergent/convergent route could be conducted (Scheme 5). Monomer 3 was divided into two parts and the first part was iodinated to afford 4 in 74% yield. The other portion of 3 was deprotected to give the 5 in 98% yield.

Coupling of 4 and 5 afforded the dimer 6 in 70% yield. The rest of the sequence proceeded in a similar fashion to afford the tetramer 7. From tetramer 7 (30 Å long) we have carried out the dimerization in an attempt to make the octameric species which is 60 Å long. However, the insolubility of the system prevented adequate characterization and it became evident that a more soluble system would be needed if we were to ultimately synthesize the desired 16-mer. Therefore, we are currently investigating a similar synthesis with other side chains that would enhance the

Scheme 5



solubility properties at the larger oligomeric stages.

In conclusion, we have developed a synthetic sequence that allows the rapid formation of some well-characterized oligomers of known constitution and length for use in nanofabrication technology. This novel divergent/convergent procedure should be amenable to other such systems.

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